

2

ADDRESS

DELIVERED AT THE THIRD ANNUAL GENERAL MEETING
OF THE

Society of Chemical Industry,

*in the Lecture Theatre of the Literary and Philosophical Society
of Newcastle-on-Tyne,*

JULY 9th, 1884,

By the Retiring President,

WALTER WELDON,

FELLOW OF THE ROYAL SOCIETY OF LONDON,
FELLOW OF THE ROYAL SOCIETY OF EDINBURGH,
FELLOW OF THE CHEMICAL SOCIETY,
FELLOW OF THE INSTITUTE OF CHEMISTRY,
MEMBRE DE LA SOCIÉTÉ CHIMIQUE DE PARIS,
CHEVALIER DE LA LÉGION D'HONNEUR,
ETC., ETC.

PRINTED FOR PRIVATE CIRCULATION.

LONDON:
ROBERTS & LEETE, SOUTHWARK, S.F.;
AND LIME STREET SQUARE, E.C.

1884.



LONDON:
ROBERTS & LEETE, SOUTHWARK, S.E.,
AND LIME STREET SQUARE, E.C.



ADDRESS, ETC.

I TRUST that it will not be unfitting that the observations which it is now my duty to offer should be devoted exclusively to that one of the chemical industries of which the district in which we are now met is so important a centre, which was first practised in England within four miles of this building, and with which it happens that I am more familiar than with any other. Eighteen months ago, before the London Section of our Society, I sketched the then present condition of that industry, and indulged in some speculations as to its future. "Many things," however, "have happened since then;" and among them have been changes, alike in the actual condition of the older branch of the Soda Industry, and in the data for estimating the probable future of that industry at large.

Since I collected, towards the end of 1882, the statistics with respect to the Soda Industry which I presented to our London Section in January last year, the ammonia process has continued its victorious advance, and the production of Leblanc soda has still further diminished. That further diminution in the production of Leblanc soda was indeed inevitable; but, whereas one expected that it would involve the

closing of more Leblanc soda works: temporarily, at any rate, this result has been avoided by combinations among Leblanc soda makers to reduce production. These combinations have been regarded as simply combinations to force up the price of certain products; but there is no room to doubt that the rise which has taken place in the price of the products in question, as a consequence of these combinations, must necessarily have taken place by this time, if those combinations had not been formed. The manufacture of chlorine and Leblanc soda, without profit, and in many cases at a loss, could not have gone on much longer. It must soon have resulted in the forced withdrawal of the weaker manufacturers from a hopeless struggle; and the effect upon prices of diminished production brought about in this way would of course have been the same as that of diminished production brought about by mutual agreement. The stronger of the manufacturers might well have preferred a continuance of the struggle until all the weaker had gone to the wall; but the consumer has certainly no cause to complain of an arrangement: the faint flavour of socialism about which renders it none the less acceptable in at least my eyes: by which,—instead of the complete closing of more works, and the ruin of their owners, the other works remaining in full activity and reaping the whole benefit of the reduced production thus occasioned,—on the one hand, the reduced production which must have been brought about in some way, and, on the other, the benefit of the higher prices resulting from it, are shared, as equally as may be,

among the proprietors of all the works which were still in operation when that arrangement was made.

While, however, the makers of soda by the Leblanc process are to-day in the position, to which they had so long been unaccustomed, of being able, not only to make both ends meet, but also, I trust, to make one end somewhat overlap the other,—what of the future of that process? Regarded merely as a means of manufacturing soda, it has served its time. Per given quantity of soda yielded by it, it is more than seventy per cent. more costly than the ammonia process; and thus its only claim to continue to live consists in the fact that it yields hydrochloric acid. So far as one can yet see, the world must continue to be supplied with chlorine. At present, the immediate raw material of the chlorine manufacture is always hydrochloric acid; and for our supply of that raw material we are entirely dependent on the Leblanc process. Is this state of things destined to continue? Is the Leblanc process likely to remain our only means of obtaining hydrochloric acid? And, above all, must the production of hydrochloric acid always be, as now, an essential condition precedent of the production of chlorine?

How to obtain, in an useful state, the chlorine, at present thrown away as calcium chloride, of the salt which is decomposed by the ammonia process, is a problem which has long occupied many minds. When it became known, in the course of last year, that Mr. Mond had patented a process to that end, it was widely felt that the solution of this problem had probably been reached; and Mr. Mond's very

ingenious process certainly would, under given conditions, enable the manufacturer of ammonia soda to utilize both the constituents of the salt which he decomposes. Mr. Mond himself, however, has never regarded this process as other than a process for the future. It is a process which would involve that the ammonia employed in the manufacture of ammonia soda, instead of being continually regenerated and used again as at present, should be used as a reagent in that manufacture only once, and should then be sold as ammonium sulphate; and hence the conditions for its extensive application obviously do not at present exist.

The form of Mr. Mond's process is due to a fact of which, until he discovered it, chemists were not aware. We know that when sodium chloride is heated with an equivalent of sulphuric acid, as in the first operation of the Leblanc process, the sulphuric acid reacts on only one-half of the sodium chloride, the products of its reaction thereupon being HCl and hydrogen sodium sulphate; but that afterwards, at a higher temperature, that hydrogen sodium sulphate reacts on the other half of the sodium chloride, another HCl being evolved, and the whole of the sodium present being converted into normal sulphate. It has been generally supposed that if ammonium chloride were substituted for sodium chloride, things would go in a similar way; but Mr. Mond has found that this is not the case. He has found that when ammonium chloride and acid ammonium sulphate are heated together, no reaction takes place between them, at whatever temperature. Below a certain temper-

ature, nothing happens; above that temperature, all that happens is that ammonium chloride volatilizes. That this fact remained to be discovered in 1883, surely shews that, in the search for new organic compounds in which chemists for so many years past have been so absorbed, the pursuit of inorganic chemistry has been somewhat unduly neglected.

When the residual liquor of the ammonia soda process has been treated for the distillation off from it of such part of its ammonia as is combined with carbonic acid, together with such of it, if any, as may be in the free state, what remains is a nearly saturated mixed solution of ammonium and sodium chlorides. On evaporating this mixed solution, its sodium chloride, being the less soluble of the two salts contained in it, falls, and may be fished out: leaving eventually a mother-liquor consisting of solution of ammonium chloride only. Mr. Mond's proposed process consists in separating in this way the sodium chloride of the mixed solution in question; in then evaporating the mother-liquor to dryness, so as to obtain solid ammonium chloride; and in then treating this solid ammonium chloride by enough sulphuric acid to form acid ammonium sulphate, $\text{H}\cdot\text{N}\text{H}_4\text{SO}_4$, the chlorine of the ammonium chloride going off as HCl . The residual acid ammonium sulphate is then either to be treated by vapour of free ammonia, and so converted into normal ammonium sulphate, for sale as such, or it is to be used, instead of free sulphuric acid and normal ammonium sulphate, in the manufacture of richly ammoniacal phosphatic manures.

If one wished to convey an idea of the stupendous

scale upon which ammonia soda is now manufactured, I think one could not do it better than by pointing out some of the conditions which would be necessary to the application of this process to the whole of the ammonium chloride produced by a single ammonia soda maker: Mr. Mond himself. It is no secret that Mr. Mond manufactures fully 50,000 tons of ammonia soda per annum. To treat the whole of the ammonium chloride corresponding to this quantity of ammonia soda by that form of the process in question in which the acid ammonium sulphate at first produced should be afterwards converted into normal ammonium sulphate by means of free ammonia, would require, not only that he should manufacture per annum 128,000 tons of ammonium sulphate, but also that he should command a constant supply of one-third more ammonia than the total quantity at present produced in all Great Britain and Ireland; while to treat that vast quantity of ammonium chloride by the form of his process in which the acid ammonium sulphate intermediately produced should be employed to react on calcium phosphate, he must manufacture per annum a quantity of manures containing 64,000 tons of ammonium sulphate, which quantity of manures could not, I believe, be less than 350,000 tons, or 40 tons for every hour in the whole year, and the production of which would require a supply of ammonia equal to two-thirds of the total quantity at present produced in all the gas works of the United Kingdom. It would involve the annual consumption of a quantity of ammonia, the production of which in gas works at present requires the distillation of five millions of tons

of coal, and the concentration of which, as gas-liquor, upon any one spot, would require that gas-liquor should come pouring in there at the rate of from a ton to a ton-and-a-half per minute, night and day, week-days and Sundays, all the year through.

Obviously,—and, as I have said, I know that this is Mr. Mond's own view,—this process cannot be extensively applied so long as we continue dependent for our supply of ammonia mainly on the distillation of coal for the manufacture of illuminating gas; and cannot, indeed, be applied on any serious scale at all except in proportion as means are realized of obtaining as ammonia the nitrogen of coal used as fuel, and as those means are practised in the immediate neighbourhood of ammonia soda works. Such means doubtless will be realized; but very much will happen before the supply of ammonia becomes so abundant as to permit the ammonia soda maker to use his principal reagent only once and then to sell it; and when that time at length arrives I think he will have no temptation to treat his ammonium chloride by sulphuric acid, but if he desires to sell his ammonia, after having used it only once, will probably best find his account in selling it in the form in which his soda process yields it. Meanwhile, I believe that Mr. Mond is not only not preparing to put this process into operation, on any scale whatever, but has no immediate intention of doing so.

An idea for the obtainment of hydrochloric acid in connection with the ammonia process, which has found more favour in many eyes than I think it deserves, and has recently been the subject of very

much experiment, is one involving a modification of the ammonia process itself, by the substitution of sodium sulphate for sodium chloride as its starting point. The idea is to first decompose salt by sulphuric acid, and so obtain hydrochloric acid and sodium sulphate, as in the Leblanc process at present, and then to treat that sodium sulphate by ammonia and carbonic acid. The experiments which have been made in this direction at least place beyond doubt: what before was widely disbelieved: namely, that a sulphate of soda ammonia process, whatever its commercial merits or otherwise, is in itself perfectly practicable. The lower solubility, in water at ordinary temperatures, of sodium sulphate than of sodium chloride, has been supposed to be an obstacle to the realization of such a process; but there is no inconvenience in employing, in the operation of decomposing sodium sulphate by bicarbonate of ammonia, a temperature of about 34° C., and at that temperature sodium sulphate is more soluble than sodium chloride: so that it is quite practicable to obtain, by treating by CO_2 an ammoniacal solution of sodium sulphate, more bicarbonate of soda than can be obtained by the corresponding treatment of an equal volume of ammoniacal brine. It has also been supposed that only one-half of the sodium sulphate treated by ammonia and carbonic acid would undergo decomposition, the second half of it going to form, with the ammonium sulphate resulting from the reaction of bicarbonate of ammonia on the first half it, double sulphate of sodium and ammonium; but experience has proved that this is not so. Nor does the regeneration of ammonia by

means of lime from the ammonium sulphate of the mother-liquor of a sulphate of soda ammonia process present any difficulty. The operation cannot be performed, owing to the formation in it of solid and bulky calcium sulphate, in precisely the same manner as the corresponding operation of the present form of the ammonia process; but means have been found of effecting it with an ease and completeness which leave nothing to be desired. It has been found, too, that calcium sulphate can be readily separated from so much of the residual solution, containing a good deal of sulphate of soda, in which it is at first suspended, that,—the separated solution being used to dissolve the next quantity of solid sodium sulphate entering the process,—the loss of sodium sulphate in a sulphate of soda ammonia process need be only extremely small. It seems quite clear, therefore, that such a process would present no practical difficulty whatever.

But, *cui bono?* To merely substitute for the Leblanc method of decomposing sodium sulphate its decomposition by bicarbonate of ammonia, would surely be a game not worth the candle. In the Leblanc process, as in so many other things, *c'est le premier pas qui coûte*. It is the first operation of the Leblanc process which makes that process so costly. It is the cost of his sodium sulphate which places the maker of Leblanc soda at such a disadvantage as compared with the maker of ammonia soda. If sodium sulphate cost the former no more than salt costs the latter, it is Leblanc soda, and not ammonia soda, which would be the cheaper of the two: since the cost of manufacturing Leblanc soda from sodium sulphate is appreciably less

than the cost of manufacturing ammonia soda from salt. The treatment of sodium sulphate by ammonia and carbonic acid would at least not be less costly than the treatment of sodium chloride by the present form of the ammonia process; and hence to merely substitute for the Leblanc method of decomposing sodium sulphate the method of decomposing it by bicarbonate of ammonia would be to substitute for the later operations of the Leblanc process a series of more costly operations, having no advantage beyond one of scarcely appreciable commercial value: that of yielding a more concentrated product.

While, however, the only advantage of a process which should consist in manufacturing sodium sulphate as in the Leblanc process at present, and then decomposing that sodium sulphate by bicarbonate of ammonia, would thus be one which would not be worth the cost of obtaining it: a process, based on the decomposition of sodium sulphate by bicarbonate of ammonia, has recently been devised, which stands upon a very different footing. In the process to which I now refer, the sodium sulphate to be afterwards decomposed by bicarbonate of ammonia would be obtained, and hydrochloric acid at the same time, without consumption of sulphuric acid, except to make up mechanical loss, by means of one and the same quantity of sulphuric acid continually regenerated and used again.

This remarkable process is the invention of three members of the firm of Gaskell, Deacon & Co., of Widnes: Mr. Carey, Mr. Holbrook Gaskell, junr., and Dr. Hurter. These gentlemen have found a means of

so decomposing ammonium sulphate as to obtain, not only its ammonia in the free state, but also its sulphuric acid, if not as free sulphuric acid, at any rate in a state in which it can decompose sodium chloride.

Chemists have long known that when ammonium sulphate is heated to a certain temperature one-half of its ammonia is set free and flies off, the other half of it remaining behind as hydrogen ammonium sulphate. Messrs. Carey, Gaskell and Hurter have discovered that if a mixture of equivalent quantities of ammonium sulphate and sodium sulphate be heated to fusion, and steam be injected into the liquid mass, the whole of the ammonia of the ammonium sulphate is disengaged in the free state: its sulphuric acid combining with the sodium sulphate to form hydrogen sodium sulphate, which alone remains behind.

Upon this most interesting reaction there may obviously be based a soda process which should begin by obtaining sodium sulphate and hydrochloric acid by the reaction of "bisulphate of soda" on sodium chloride, the normal sodium sulphate so obtained being then decomposed by bicarbonate of ammonia, with production of bicarbonate of soda and ammonium sulphate, such ammonium sulphate being then so treated as to regenerate, by one and the same operation, both ammonia for use again, and bisulphate of soda for use again.

The question of whether or not this most original and beautiful process can be reduced to practice must obviously depend, mainly if not solely, upon the degree of readiness with which the new reaction upon which

it is based can be carried to such completeness as to avoid any serious loss of ammonia. I am unacquainted with the experimental results on this point which have so far been obtained; but it is easy to see that that reaction might be somewhat slow, and, therefore, somewhat costly, and yet the process based upon it be one of very serious importance.

Charging against the hydrochloric acid yielded by Messrs. Carey, Gaskell and Hurter's process, the cost of those operations of their process which are in excess of the operations which the ammonia soda maker performs at present, one may count that the cost of their soda would be practically the same as that of ammonia soda as at present manufactured from brine. Their process would start from solid salt, which is, of course, more costly than brine; but, in some localities, at any rate, the value of the lime which is required for the decomposition of the ammonium chloride of the present form of the ammonia process, but which would not be required in Messrs. Carey, Gaskell and Hurter's process, would fully compensate the greater cost for raw materials of the latter than of the former.

The operations, the cost of which would thus have to be charged against Messrs. Carey, Gaskell and Hurter's hydrochloric acid, are those: firstly, of evaporating to dryness the mixed solution of ammonium sulphate and sodium sulphate constituting the mother-liquor of the bicarbonate of soda obtained by treating an ammoniacal solution of sodium sulphate by carbonic acid; secondly, of treating the residue of that evaporation, after addition to it of more sodium sulphate, for the regeneration of ammonia and the

production of bisulphate of soda ; and, thirdly, of then furnacing that bisulphate of soda with an equivalent quantity of salt.

The quantity of water which would have to be evaporated, in the first of these three operations, per ton of sodium carbonate manufactured, may be put, I believe, at five-and-a-half tons. It would be the water of a mixed solution of ammonium sulphate and sodium sulphate, and as these are both salts which, like sodium chloride, absorb heat during solution in water, and so give out heat during the inverse operation,—the two together, in the proportions in which they would be present in the solution in question, to just about the same extent as sodium chloride,—it ought to be possible to evaporate those five-and-a-half tons of water by means of the one ton of fuel which suffices for the evaporation of more than that quantity of water from brine. For the third operation, which would correspond to the second half of the first operation of the Leblanc process, less than half-a-ton of fuel should be ample. The labour upon these two operations would obviously be but slight, so that the cost of both operations together, for fuel and labour, per ton of sodium carbonate manufactured, could scarcely, I think, exceed eleven or twelve shillings.

The quantity of hydrochloric acid which corresponds to the quantity of sodium chloride corresponding to a ton of sodium carbonate, counted as aqueous acid of 27 per cent., is 2·548 tons. There are some Leblanc soda works in which the proportion of the total HCl evolved therein, which is obtained as aqueous acid of

useful strength, is fully 95 per cent. Assuming this proportion of the HCl evolved in Messrs. Carey, Gaskell and Hurter's process to be obtained in an useful form, the process would yield, per ton of sodium carbonate manufactured by it, a quantity of aqueous acid corresponding to 2.42 tons at 27 per cent.

The value of this quantity of hydrochloric acid I estimate at £2 8s., and I arrive at that value for it in this way. The difference between the cost of ammonia soda and that of Leblanc soda, *plus* hydrochloric acid, per quantity of Leblanc soda equivalent to a ton of ammonia soda, now averages, I believe, in England, about £2 15s. These £2 15s. I take to be the value, in the sense of the actual cost, not of the quantity of hydrochloric acid, of useful strength, which is usually obtained concurrently with that quantity of Leblanc soda, but, what is by no means the same thing, of the greatest quantity of such acid which is obtained, per such quantity of soda, in any instance within my knowledge. This quantity,—for we must remember that the Leblanc soda maker has to produce more sodium sulphate, and, consequently, more hydrochloric acid, than merely the quantity equivalent to the alkali he finally obtains,—is 95 per cent. of the quantity corresponding to about twelve-and-a-half per cent. more sodium sulphate than the quantity of sodium sulphate equivalent to a ton of sodium carbonate, and is thus, counted as acid of 27 per cent., almost exactly two-and-three-quarter tons: £2 15s. for which quantity is just £1 per ton, or £2 8s. for the 2.4 tons which I have taken to be obtainable, by the process under consideration, per ton of sodium carbonate manufactured thereby.

Taking it, then, that the minimum present cost of aqueous hydrochloric acid of 27 per cent. is £1 per ton; that Messrs. Carey, Gaskell and Hurter's process could yield, per ton of sodium carbonate manufactured by it, 2·4 tons of such acid, thus worth at least £2 8s.; and that, of the three operations the cost of which would have to be charged against those 2·4 tons of hydrochloric acid, twelve shillings would pay for two: there would thus remain £1 16s., the balance left after the deduction from which sum of the cost of effecting Messrs. Carey, Gaskell and Hurter's reaction on about 2 tons 12 cwt. of a mixture of ammonium sulphate and sodium sulphate, would be the measure of the advantage of their process over the Leblanc process.

It is so difficult to conceive that the cost of effecting the reaction in question upon the quantity of materials which I have mentioned could be anything like £1 16s., that for this process of Messrs. Carey, Gaskell and Hurter's I could not but anticipate a most important future: were it not for the results of a renewed attempt which has for some time past been in progress to realize the old idea of decomposing the ammonium chloride of the present form of the ammonia process by magnesia, and then so treating the resulting magnesium chloride as to obtain its chlorine in an useful form and at the same time to regenerate magnesia for use again. In this method of procedure there would be one operation less than in Messrs. Carey, Gaskell and Hurter's process: the operation of evaporation, which would be practically the same in both processes, being followed, in Messrs. Carey, Gaskell and Hurter's process by two operations, in the first of

which there would be treated, per ton of sodium carbonate manufactured, about 52 cwt. of mixture of sodium sulphate and ammonium sulphate, and in the second about 68 cwt. of mixture of sodium chloride and hydrogen sodium sulphate, while, in what may be called the magnesia process, the operation of evaporation would have to be followed by simply the one operation of decomposing about eighteen-and-a-half hundredweight of magnesium chloride. To which must be added the far graver consideration that while Messrs. Carey, Gaskell and Hurter's process can yield the chlorine of the salt treated by it only as hydrochloric acid, a large part of the chlorine of magnesium chloride can be obtained directly in the free state.

It is MM. Pechiney et Cie., of Salindres, in the south of France, who have had the boldness to attack again the problem,—upon which so many earnest workers had spent in vain their utmost efforts during many years,—of how to obtain, as magnesium chloride, the chlorine of the salt decomposed by the ammonia process; and their genius and skill have enabled them to reach results which compel the conviction that the industrial realization of the decomposition by magnesia of the ammonium chloride of the ammonia process is now only a question of time.

If, then, the manufacturer of ammonia soda shall become able, as he certainly will become able, to obtain as magnesium chloride the chlorine which he at present throws away as calcium chloride: how is that magnesium chloride to be dealt with? When an aqueous solution of magnesium chloride is subjected to evaporation, vapour of hydrochloric acid begins to be

disengaged so soon as the quantity of water present has fallen to six equivalents, per equivalent of magnesium chloride. Fifteen or sixteen years ago, at the Gerard's Bridge Works of Messrs. J. C. Gamble & Son, of St. Helens, very considerable quantities of solution of magnesium chloride, concentrated to that point, were treated in muffle furnaces. The magnesium chloride was readily enough decomposed, but the furnaces were rapidly destroyed: by reason of the concentrated solution fed into them penetrating their beds, and causing the beds to "rise." The Gerard's Bridge experiments on the decomposition of magnesium chloride were therefore abandoned; but not until they had proved that the difficulties in the way of decomposing that compound industrially by heating it in an atmosphere of vapour of water, were simply mechanical difficulties.

Seeking, during many years subsequently, means of treating by heat and air, under industrial conditions, chlorides of various metals, I was at length led, in 1881, to the idea of adding to a concentrated solution of a chloride or mixture of chlorides, oxide of the same metal or metals, and then treating by heat and air solid masses of the resulting mixture: and since early in 1882, MM. Pechiney et Cie. have been earnestly engaged in endeavouring to realize this method of working: especially as applied to magnesium chloride, enormous quantities of which they obtain as a by-product of the manufacture of salt from sea-water, and also to manganese chloride. In the case of magnesium chloride, the product of the addition to its aqueous solution of magnesium oxide is, of course, not

a mere mixture, but the compound, magnesium oxychloride. I had found in the laboratory that this body, heated in contact with air under certain conditions, gives off an appreciable part of its chlorine in the free state; and the larger experiments which have since been made at Salindres leave no doubt that fully half the chlorine of magnesium chloride may be obtained directly as free chlorine by converting the magnesium chloride into oxychloride, and then heating that oxychloride, under certain conditions, in presence of air. What this means is that a manufacturer of ammonia soda, able to decompose his ammonium chloride by magnesia, will be able, by evaporating, per ton of ammonia soda manufactured, a quantity of solution of magnesium chloride containing about five-and-a-half tons of water, and then heating in presence of air a mixture of about eighteen-and-a-half hundredweight of magnesium chloride with about eight hundredweight of magnesia, to obtain the quantity of free chlorine corresponding to very nearly a ton of bleaching-powder,—being the quantity of chlorine the present cost of which, as I shall show in a moment, is close upon £6.—and, in addition, a quantity of hydrochloric acid corresponding to something over a ton of aqueous acid of 27 per cent. The chlorine obtained by heating magnesium chloride in contact with air is of course diluted by other gases; but MM. Pechiney et Cie. have in operation an extremely simple mechanical bleaching-powder chamber, the complete absorption in which of the chlorine of a mixture of chlorine and other gases presents no difficulty.

The two questions which I asked some time ago I

have now answered. Clearly, the Leblanc process is not destined to remain our only means of obtaining hydrochloric acid; and for my own part I can have no doubt that the use of hydrochloric acid as the immediate raw-material of the chlorine manufacture is also one of those things in respect of which the old order must,—partially, at any rate,—give place to new.

And I ought to add that the processes for the obtainment of chlorine and hydrochloric acid in connection with the manufacture of ammonia soda which I have mentioned, are not the only processes to those ends which are in the field. Within the last few weeks, M. Solvay has taken three more patents for such processes; and quite a number of other workers at the problem of obtaining chlorine or hydrochloric acid from calcium chloride now consider that they are on the verge of success.

While, however, it is now quite certain that chlorine will be manufactured at least from magnesium chloride, one can hardly conceive that its manufacture from either magnesium chloride or calcium chloride can ever more than partially displace its manufacture from hydrochloric acid: whatever changes may take place in our mode of obtaining hydrochloric acid. I come now, therefore, to the question of the utilization of hydrochloric acid in the chlorine manufacture more completely than it is utilized therein at present: a question upon which the continued existence of the Leblanc process certainly now mainly depends.

The present Weldon process, even when performed to the very best advantage, does not yield more than

one-third of the total chlorine of the hydrochloric acid treated by it: the other two-thirds of that chlorine being lost as calcium chloride. It is thus unquestionably a barbarous process. It met well enough the wants of the time when hydrochloric acid could be counted as having no value, and when the two problems in respect of the chlorine manufacture which pressed to be dealt with were simply those of how to diminish the then chief item of the cost of chlorine,—that for native manganese,—and how to keep the offensive residual product of the treatment of that native manganese by hydrochloric acid out of the water-courses; but it is no longer equal to the production of cheap bleaching-powder, now that the value of hydrochloric acid has become such that the bleaching-powder produced by it costs more for hydrochloric acid than for all other items of its cost put together. For some years past, therefore, many inventors have been endeavouring to devise a hydrochloric acid chlorine process which should yield in the free state practically the whole of the chlorine of the acid treated by it; and a process which I believe will do this is one of the group of processes to the endeavour to realize which MM. Pechiney et Cie. have for some time past been devoting not only vast material resources, but a power of overcoming the practical difficulties which are always encountered in attempts to work out new industrial chemical processes, of which I have known no parallel.

The process in question is simply a new form of a very old idea. Its first operation consists in digesting with aqueous hydrochloric acid an oxide of man-

ganese which has been regenerated from manganese chloride in the dry way. There are thus obtained undiluted chlorine, and a residual solution of manganese chloride. The latter is then evaporated to dryness, and the solid manganese chloride so obtained is then heated in intimate contact with atmospheric oxygen. The chlorine of the manganese chloride is thereby driven off in the free state,—mixed, of course, with other gases,—and its manganese obtained as an oxide, rich in oxygen, with which to recommence the round of operations. Per given quantity of hydrochloric acid treated by it, the process yields practically the same quantity of strong chlorine as can be obtained from the same quantity of acid by means of Weldon mud, together with something over twice that quantity of chlorine diluted by other gases.

I shall, certainly, at least not be above the mark if I take the consumption of hydrochloric acid, per ton of bleaching-powder made by the present Weldon process, at the quantity, the production of which by the Leblanc process, together with the quantity of soda which must be produced at the same time, costs £5 more than the cost of producing by the ammonia process the equivalent of that quantity of Leblanc soda: or, in other words, at the quantity corresponding to five tons of aqueous hydrochloric acid of 27 per cent. I know of no instance in England in which a ton of Weldon bleach is obtained per less than 5·7 tons of such acid; but I propose to assume that a ton of bleaching-powder can be made, by the present Weldon process, per the quantity of acid, the present minimum cost of which is £5.

The other items of the cost of a ton of bleaching-powder, made by that process,—apart from lime for the chambers, labour on the chambers, casks, packing, and general charges,—are those for lime for the oxidizers, limestone or chalk for the wells, manganese to make up loss, fuel, labour on the stills, and labour on the regeneration process. I believe that the sum of these items averages about 19s. : bringing up to about £5 19s. that part of the expense of manufacturing a ton of bleaching-powder by the present Weldon process which represents the cost of that ton of bleaching-powder for chlorine only.

The process which is now on the point of being got to work at Salindres, after much experience of it on a semi-industrial scale, requires neither lime nor limestone, nor does one see how there can be any appreciable loss of the manganese employed in it. The loss of manganese incurred in the present Weldon process is mainly due to impurities which are constantly entering that process, and have to be continually eliminated and thrown away, and with which it is impossible to avoid throwing away more or less manganese; but in the new process in question there is nothing to throw away. Its cost is thus simply for acid, fuel, and labour.

That that process is capable of yielding the quantity of chlorine corresponding to a ton of bleaching-powder, per quantity of hydrochloric acid corresponding to less than 30 cwt. of acid of 27 per cent., is already sufficiently demonstrated. The value of that quantity of acid being taken at £1 10s., there remains £5 19s., less £1 10s., or £4 9s., out of which to pay

simply the cost of evaporating to dryness a quantity of solution of manganese chloride containing one-and-three-quarter tons of water, and then treating by heat and air something less than fifteen hundredweight of manganese chloride mixed with a certain proportion of manganese oxide. The advantage of the new process over the old one, per ton of bleaching-powder manufactured, will be the balance left after deducting from those £4 9s. the cost of these two operations.

The difficulties which have been encountered in the endeavour to realize this process have been mainly with respect to the apparatus and mode of working by which to effect the often proposed reaction of atmospheric oxygen upon manganese chloride. Manganese chloride is a somewhat readily fusible salt; oxygen does react upon it below its fusing point, but only slowly; for the reaction to go on sufficiently rapidly, the temperature employed must be above the fusing point of the manganese chloride, and the latter must present to the air by which it is treated a very considerable surface; while a fused mass of manganese chloride not only presents far too small a surface, but is destructive of all materials of which apparatus for treating it industrially could be formed.

For the treatment of manganese chloride, as of magnesium chloride, the principle adopted at Salindres is that, to which I have already referred, of mixing the chloride to be treated by heat and air with an oxide of the same metal: the main function of the oxide being to mechanically divide the chloride, so as to permit of the chloride being heated to above its fusing point, without the mass treated becoming fluid.

or ceasing to be penetrable by air. I will not stay to describe the various ingenious appliances which MM. Pechiney et Cie. have successively devised for the performance of the operation of treating by heat and air mixtures of manganese chloride and manganese oxide; but will only add that I believe that they have now completely overcome all the many difficulties which for a long time seemed to render the industrial realization of that operation almost hopeless, and that it now seems certain that they will soon be manufacturing chlorine from the hydrochloric acid of the Leblanc process at the rate of the quantity of chlorine corresponding to a ton of bleaching powder per little more than fourteen hundredweight of salt.

Given this result: a result diminishing by two-thirds the quantity of Leblanc soda necessary to be manufactured in order to the manufacture of a given quantity of chlorine from Leblanc hydrochloric acid: will it enable the Leblanc process, thus shorn of its proportions, to continue to live, in face of the decomposition by magnesia of the ammonium chloride of the ammonia process, and the direct obtainment from the resulting magnesium chloride of one-half of its chlorine in the free state? I trust that this may be so; but, as yet, the data for a conclusion on the point are insufficient, and of those of them which as yet exist, some tell one way, and some the other. The manufacture of chlorine from magnesium chloride, obtained by decomposing by magnesia the ammonium chloride of the ammonia process, involves much more evaporation than is required for the manufacture of the same quantity of chlorine from

hydrochloric acid by the process to which I have just referred ; and the whole of the chlorine obtained by the former process is diluted by other gases, whereas one-third of the chlorine obtained by the latter process is undiluted. On the other hand, the degree of dilution of the chlorine obtained from magnesium chloride is somewhat less than that of the chlorine obtained from manganese chloride ; and to decompose magnesium chloride, or rather magnesium oxychloride, by heat and air, is somewhat easier than to decompose manganese chloride by the same means. All that is yet clear in the matter therefore is that chlorine will be manufactured in connection with the ammonia process, though perhaps not to any appreciable extent for a few years yet. But the question which, in face of that certainty, it is impossible not to ask : the question of whether it is or is not likely that the greatest chemical invention of the eighteenth century, if not indeed of any century, shall have ceased, by the end of the nineteenth, to be anything more than a tradition and a name : as yet it is equally impossible to answer.

If, however, unfortunately, that question shall be eventually answered in a sense adverse to those whose capital is invested in the Leblanc process : must the manufacture of soda disappear from Tyne-side ? It was on Tyne-side that “ artificial soda,” as it used to be called, was first manufactured in England : must, in such case, this district know that industry no more ? I am not of that opinion. At present, the manufacturer of ammonia soda from brine employs, per ton of soda manufactured, from a

ton and a quarter to a ton and a half of coal, and the quantity of brine containing about forty-six hundred-weight of salt. His coal consumption is thus light, but the quantity of salt which he consumes is twice the quantity equivalent to the soda he manufactures. Any method, however, of obtaining, either as free chlorine or as hydrochloric acid, the chlorine of the salt decomposed by the ammonia process, must necessarily involve the evaporation of all the water employed in that process,—during which evaporation that portion of the salt employed in it which at present escapes utilization will be recovered,—and must moreover involve a subsequent operation, also requiring an expenditure of fuel. Any such method must thus reduce to absolutely its theoretical amount the quantity of salt consumed in the ammonia process, per unit of soda manufactured thereby, reducing it to one-half the quantity at present required by the manufacturer of ammonia soda from brine, but must at the same time increase his consumption of coal, per unit of soda, by at least between one hundred and two hundred per cent. Under such changed conditions: at any rate when Cleveland salt shall have become obtainable here at a cost not much greater than that of Cheshire salt in Lancashire: I think it ought to be possible to manufacture ammonia soda in this district very nearly if not quite as cheaply as in any other locality whatever.

It is not willingly that I have announced a new—and much more serious than any previous—menace to an industry already sorely tried. How much I should have preferred to have been able to prophesy smooth

things with respect to the Leblanc process, no words can say. Facts, however, must be looked in the face. Nothing can be less wholesome than the atmosphere of a fools' paradise. And the watch-dog at the gate, who gives timely notice of the approach of unwelcome visitors, at least renders such service as is in his power.

But if such changes as that which I have indicated as now certain to be accomplished at least partially are unwelcome, it is only in so far as they may affect individuals. By such changes, individuals may, and alas! do suffer; but the world gains by them. No industrial process is ever superseded, however partially, excepting by a better process. And in so far as the Leblanc process may be doomed to still further restriction, it can only be because some other process can give mankind cheaper soda and cheaper chlorine than it can give.

And the various proposed new processes of which I have spoken all comply with at least one of the ideals towards which all progress in such matters must henceforth tend. They all possess in common one feature which will certainly be held essential to all industrial chemical processes in a not distant future. They are all processes yielding no waste product. They are all processes completely utilizing all the constituents of all their raw materials. Excepting coal and water, nothing would be manipulated in any of them which was not finally yielded either as commercial commodity, or as regenerated reagent for use again. That way certainly lies the future.

Amongst the many transcendent merits of the

beneficent invention of Nicolas Leblanc, of immortal memory, that of yielding no waste product is not included. There are spots on the sun; and the Leblanc process yields alkali-waste. Countless have been the efforts to utilize at least one of the constituents of that residue; but none of them have fully succeeded. Now, however: ninety-seven years after the invention of the process to which we chiefly owe that soap, and glass, and paper, and countless other commodities only less useful than these, have been placed within the reach of all mankind; seventy-four years after its inventor, “the creator,” as Hofmann puts it, “of incalculable wealth for his species,” put an end to his existence because he wanted bread: which makes it so pleasant to know that two generations afterwards he at least received a stone—statue, towards the erection of which, however, I have yet to learn that any English soda maker contributed: now, when one cannot but fear that the long day of the Leblanc process may be tending towards its close, a means of utilizing both the principal constituents of that residue seems almost in sight. To speak now of the recovery of sulphur from Leblanc soda waste may seem a kind of anti-climax; but the gallant attempt to realize the Schaffner and Helbig process to that end upon which Mr. Alexander Chance recently expended so much enthusiastic effort, and the firm of which he is a member the greater portion of £10,000, has not only resulted in a reduction in the price of pyrites, but also in the suggestion of various other processes for the accomplishment of the same object: to a conceivable combination of certain parts of some of which I would

ask permission to devote a very few concluding sentences.

The combined process in question would commence by bringing the calcium sulphide of alkali waste into solution as calcium sulphhydrate, by treating a mixture of waste and water by sulphuretted hydrogen. The second operation would consist in evaporating the resulting solution of calcium sulphhydrate, and so driving off its sulphur as pure H_2S ; and the third and final operation in burning off the hydrogen only of that sulphuretted hydrogen, setting its sulphur free.

The third of these operations has for some time past been under experiment in the works of Messrs. Chance Brothers, at Oldbury. The apparatus used in it is one invented by Mr. C. F. Claus, of London, and consists of a kiln in which there is a deep bed of fragments of porous material, through which, when the apparatus is at work, there is passed a mixture of sulphuretted hydrogen with a carefully regulated quantity of air. The bed of porous material is maintained at a high temperature by the heat of the reaction which takes place as the mixture of gases passes through it, and from the mixture of gases and vapours passing off from it sulphur condenses as that mixture cools. The operation thus costs nothing for fuel, and its cost for labour is scarcely more than the cost of from time to time removing sulphur from the receptacles in which it has condensed and collected.

The first of the three operations is in industrial operation at Rassuen, in the South of France, in connection with a most ingenious process, invented by M. Lombard, of Marseilles, in which calcium sulphy-

hydrate is used to precipitate dicalcic phosphate from the solution obtained by dissolving native calcium phosphate in hydrochloric acid. It is also in operation, on a semi-industrial scale, in the alkali work of Hrůschau, in Moravia. Its cost is simply that of charging waste and water into horizontal cylinders furnished with mechanical agitators, keeping these agitators in motion during the operation, and at the end of the operation discharging the contents of the cylinders.

The second of the three operations is under experiment at Hrůschau, by Dr. Heinrich von Miller and Herr Opl. This second operation is obviously more costly than the first or third; but it yields, in addition to sulphuretted hydrogen, another product, which other product, it is hoped, may pay, nearly if not quite the whole cost of the three operations. This other product is chemically pure calcium hydrate: resulting from the reaction—



Unlike the recovered calcium carbonate of the Schaffner and Helbig process, this calcium hydrate can be readily obtained absolutely free from impurities, since no impurities precipitate with it, and its physical condition is such that water or a solution runs from a heap of it almost as readily as from so much sand. It is incapable of causticising solutions of sodium carbonate, more than partially; it is too dense for use in Weldon oxidizers; but it seems not unlikely to prove suitable for use in bleaching powder chambers.

If it should prove to be the case, on the one hand, that this dense crystalline calcium hydrate shall have

the value of an equivalent quantity of ordinary lime, and, on the other hand, that the hydrogen of sulphuretted hydrogen can be oxidized, practically completely, without at the same time oxidizing any appreciable proportion of its sulphur: then I think that an almost ideally perfect solution of the problem of the utilization of the residual product of the Leblanc process will at last have been reached. If this should be so, one can only hope that that solution will not have arrived too late.

